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Cellobiose-Based Liquid Crystals. (n-Alkyl β -D-Cellobioside) Hepta-n- alkanoates

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Cellobiose-Based Liquid Crystals. (n-Alkyl β -D-Cellobioside) Hepta-n-alkanoates

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(n-Alkyl β -D-cellobioside) hepta-n-alkanoates with varying lengths of alkyl and alkanoyl chains were synthesized via four steps starting with D-cellobiose octaacetate. These new compounds were found to form a thermotropic liquid crystalline phase of smectic type when the alkyl and alkanoyl lengths were appropriate. It was demonstrated that a rather minor difference in molecular structure, e.g., an ether vs. ester linkage at the 1-O position, could bring about a considerable difference in the temperature span or the stability of the mesophase.

KEY WORDS: Thermotropic liquid crystals/ Cellobiose derivatives/ Ether linkage/ Ester linkage/

INTRODUCTION

During the course of a series of studies on the thermotropic liquid crystals of cellulosic and oligo-cellulosic derivatives¹⁻⁴⁾, we have studied two kinds of D-cellobiose derivatives; D-cellobiose octaalkanoates (C_bOA)⁵⁾ and alkyl β -D-cellobiosides (AC_b)⁶⁾. C_bOA is a nearly symmetrical molecule with eight alkyl chains bonded to cellobiose (C_b) by an ester linkage, and AC_b is a tadpole-shaped asymmetric molecule with an alkyl chain bonded to C_b at the 1-O position. Both C_bOA and AC_b were found to form a thermotropic mesophase when the alkyl lengths were appropriate. However, their mesophase properties were very different. C_bOA 's were characterized by a smectic-type texture and a high viscosity. An X-ray diffraction study suggested its mesophase to be of columnar type⁷⁾. The AC_b mesophase had a relatively low viscosity and exhibited several characteristic textures such as transient bâtonnets, homeotropic, and focal conic, depending upon the thermal history and alkyl length. A homeotropic-to-polygonal textural transition was induced by a positive (but not negative) temperature jump applied to the homeotropic phase. Pitch-bandlike lines were often visible in the focal-conic textures. Those observations suggested that the AC_b phase is a chiral smectic C modification⁶⁾.

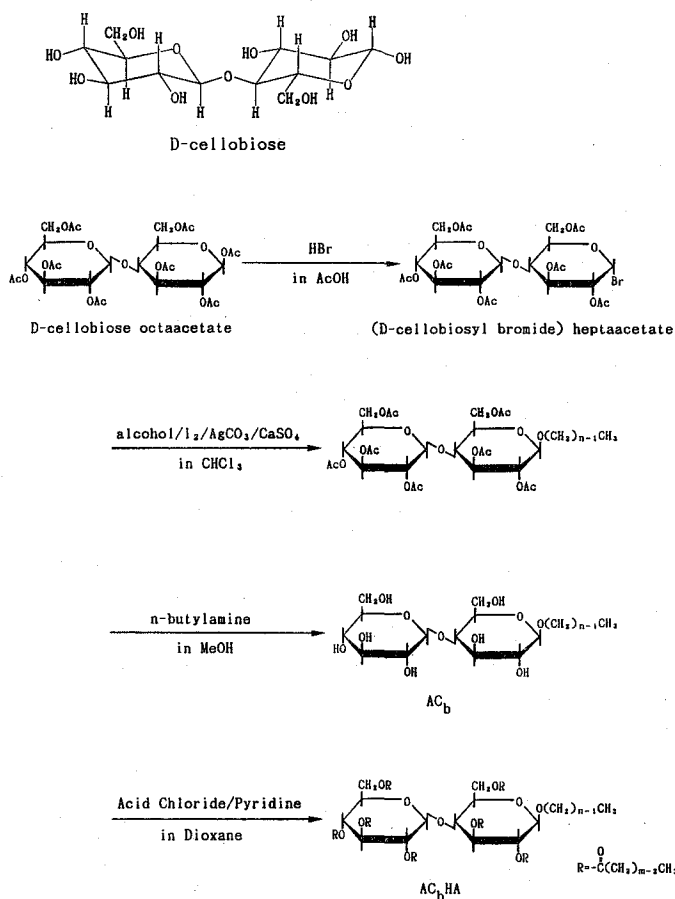
In this paper, we have synthesized a series of (alkyl β -D-cellobioside) hepta-alkanoates (AC_bHA) and studied their thermal properties. These derivatives have both O-alkyl and O-alkanoyl groups, so it would be interesting to study their mesophase properties in comparison with those of C_bOA and AC_b .

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EXPERIMENTAL

Sample Preparation AC_bHA 's were prepared by a four-step procedure that consisted of a selective bromination of *D*-cellobiose octaacetate at the reductive end, the reaction of the bromide with an alcohol, the deacetylation and the subsequent re-acylation of the alkyl cellobioside:



Scheme 1

The experimental procedure upto the step of AC_d preparation has been described elsewhere⁶⁾, which was basically the same as was given by Wolform and Haq.⁸⁾ In what follows, we describe about the final step, by taking the preparation of (n-decyl β -*D*-cellobioside) hepta-n-hexadecanoate as example.

All chemicals used were either of reagent grade or fractionally distilled prior to use. To 100 mg (0.21 mmol) of n-decyl β -*D*-cellobioside dispersed in 2 mL of dioxane were added 230 mg (2.9 mmol) of pyridine and then 540 mg (2.2 mmol) of hexadecanoyl chloride, and the system was placed in an oil bath (95°C) and refluxed under a nitrogen atmosphere. After 20 h, the system, consisting of a yellowish transparent solution and a smaller amount of a yellow-white oily material

that solidified at room temperature was poured into 50 mL of methanol/ water 10/1 mixture to have a white precipitate. The precipitate, AC_bHA , was recovered by filtration, washed several times with the methanol/ water mixture of the same composition as the above and finally with a small amount of pure methanol, and dried in vacuum thoroughly.

Measurements Infrared (IR) spectra were obtained with a JASCO FT/IR spectrometer Model 8800, Japan. Differential scanning calorimetric (DSC) measurements were made on a Rigaku Denki Model DSC-8230, Japan, at a constant heating/cooling rate of $10^\circ\text{C}/\text{min}$. Polarized optical microscopic observations were made with a Nikon Model Optiphot-Pol, along with the use of a Mettler hot stage Model FP-82, Switzerland.

RESULTS AND DISCUSSION

Two series of AC_bHA 's were prepared, which will be abbreviated as $A_{10}C_bHA_m$ and $A_mC_bHA_m$. $A_{10}C_bHA_m$'s have a n-decyl group in common and seven n-alkanoyl groups of carbon number m , while $A_mC_bHA_m$ have an n-alkyl and seven n-alkanoyl groups of common carbon number m . Figure 1 shows the FT/IR spectra of alkyl cellobioside $A_{10}C_b$ and one of its alkanoates $A_{10}C_bHA_{16}$. In the latter spectrum, the hydroxyl absorption band present in the former spectrum ($\sim 3,300\text{ cm}^{-1}$) is absent, and the carbonyl absorption band ($\sim 1,700\text{ cm}^{-1}$) is present. The elemental analysis also confirms full acylation of cellobiosides in all cases (Table I).

Both $A_{10}C_bHA_m$ and $A_mC_bHA_m$ were found to form a thermotropic mesophase when m was appropriate. Figure 2a shows the texture of the masophase of

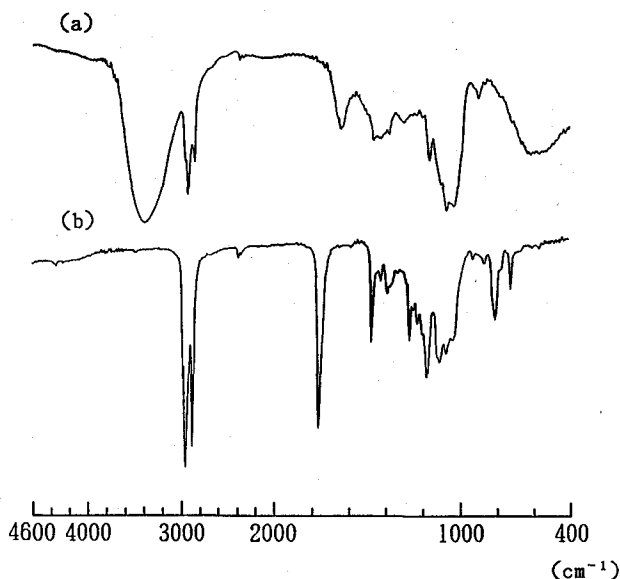


Fig. 1. FT/IR spectra of (a) n-decyl β -D-cellobioside and (b) its hepta-n-hexadecanoate.

Table I. Results of Elemental Analysis.

m	Calculated		Found	
	C(%)	H(%)	C(%)	H(%)
(n-Decyl β -D-Cellobioside) Hepta-n-alkanoate $A_{10}C_bHA_m$				
2	55.67	7.22	55.59	7.24
4	61.73	8.64	61.29	8.47
6	65.75	9.59	65.38	9.57
8	68.62	10.26	68.08	10.18
10	70.77	10.77	70.48	10.81
12	72.44	11.16	72.13	11.17
14	73.73	11.55	72.75	11.57
16	74.81	11.81	73.04	11.73
18	75.72	12.02	75.13	11.85
(n-Alkyl β -D-Cellobioside) Hepta-n-alkanoate $A_mC_bHA_m$				
8	68.26	10.18	67.85	10.20
9	69.61	10.50	68.96	10.54
10	70.77	10.77	70.48	10.81
12	71.77	11.00	72.18	11.34
14	72.65	11.21	73.41	11.66
16	73.42	11.39	74.78	12.01
18	74.10	11.55	74.11	12.09

$A_{10}C_bHA_{10}$ formed after it was made isotropic at 95°C and then cooled and maintained at 89°C. The picture shows a smectic-type texture. All other samples showed essentially similar textures to this. That this is actually a mesophase can be confirmed by the easiness of shearing the sample by, for example, pressing and sliding the cover glass, and also by a shear-induced textural change. Figure 2b shows the texture of sheared $A_{10}C_bHA_{10}$, which exhibits fine vertical lines perpendicular to the shearing direction. Generally, the textures of AC_bHA 's, once formed, are quite stable to temperature changes. Insofar as photomicroscopic observations are concerned, no essential textural change occurs by decreasing the temperature even down to the solid state.

Figures 3 and 4 show the DSC thermograms of two series of samples. For $m \leq 6$ or $m \geq 16$, $A_{10}C_bHA_m$ gives, in a cooling mode, a single endothermic peak, while for $8 \leq m \leq 14$, it gives two such peaks. All of the $A_mC_bHA_m$'s studied here ($8 \leq m \leq 18$) have two peaks. The higher-temperature peak of the two is much smaller than the lower-temperature one, which implies that the phase between the two peaks is a less ordered one than a crystal, i.e., a mesophase, as in fact has been confirmed photomicroscopically. Thus, the higher-temperature peak corresponds to the anisotropic-to-isotropic liquid-liquid transition, and the lower-temperature one, to the solid-liquid transition. Tables II and III summarize the calorimetric results.

The transition temperatures of $A_{10}C_bHA_m$ are plotted as a function of m in Figure 5, where i, a, and s denote the isotropic, anisotropic, and solid phase, res-

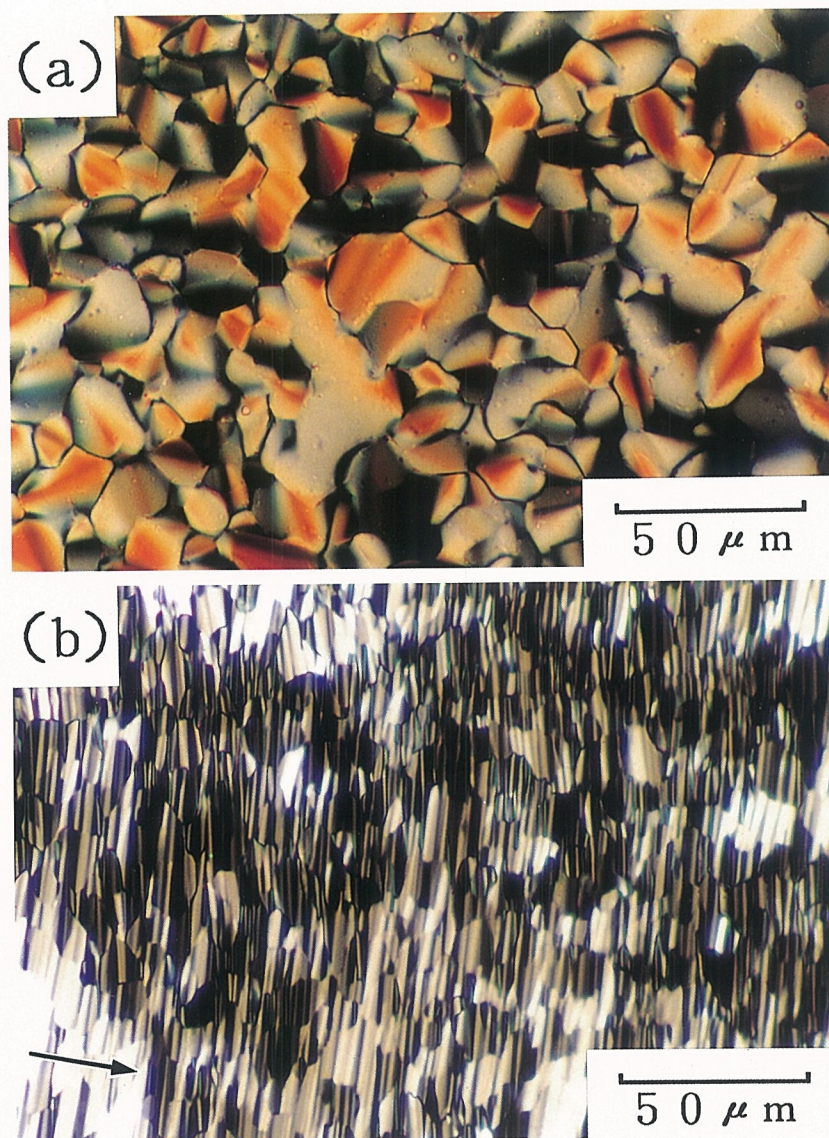


Fig. 2. Photomicrographs of A₁₀CbHAM (a) before and (b) after a shear was applied in the direction indicated by the arrowhead.

pectively. As already noted, the alkyl cellobioside forms an **a** phase that is presumed to be a chiral smectic C modification. The data points at $m=0$ in Figure 5 indicate this. When m is nonzero and small, no mesophases are formed, and the solid-liquid transition temperatures do not change significantly. Alkanoyl groups with $m \geq 8$ bring about a considerable decrease of the transition temperature and a new anisotropic phase. The **a** region observed by the cooling mode (Figure 5b) is larger than that observed by the heating mode (Figure 5b), as is usually the case.

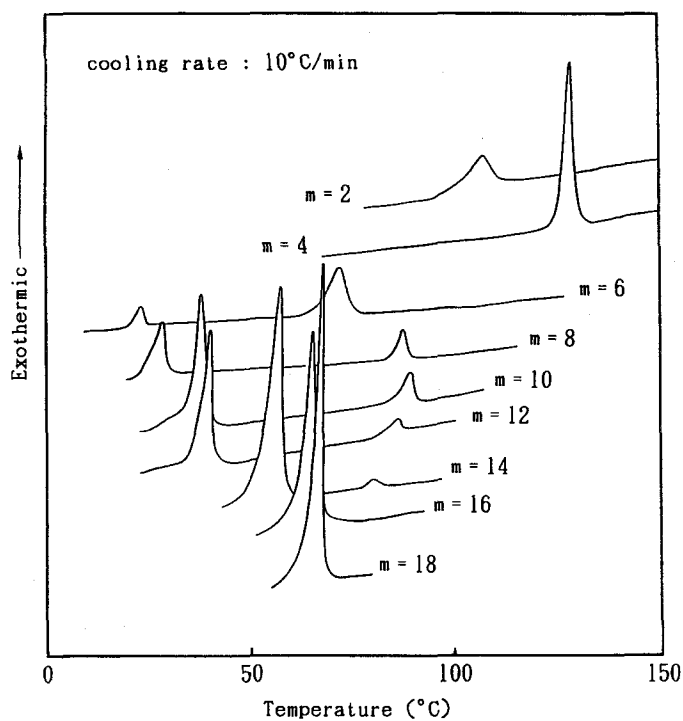


Fig. 3. DSC thermograms of $A_{10}C_6HAm$.

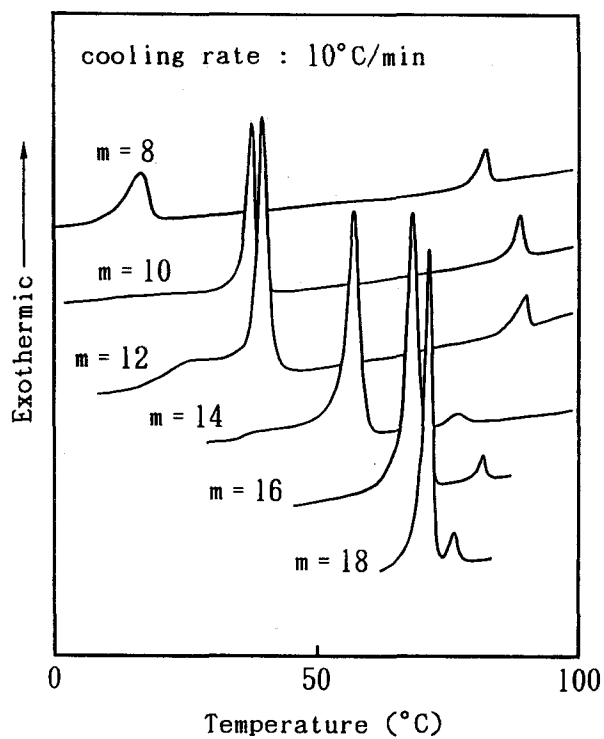


Fig. 4. DSC thermograms of A_mC_6HAm .

Cellobiose-Based Liquid Crystals

Table II. Transition Temperatures of (n-Decyl β -D-Cellobioside) Hepta-n-alkanoates $A_{10}C_bHA_m$

m	heating mode		cooling mode	
	T_{sl} ($^{\circ}C$) ^a	T_{al} ($^{\circ}C$) ^b	T_{la} ($^{\circ}C$) ^c	T_{ls} ($^{\circ}C$) ^d
0	155	227	(220)	(120)
2	144.9			
4	140.6			126.7
6	83.3			72.2
8	66.6	91.7	87.5	29.1
10	61.7	95.3	90.7	39.5
12	70.5	90.5	86.1	41.0
14	77.1	86.6	(72)	58.3
16	81.5			66.9
18	81.2			67.1

^a Transition temperature from a solid to an isotropic or anisotropic liquid.

^b Anisotropic liquid-to-isotropic liquid transition temperature.

^c Isotropic liquid-to-anisotropic liquid transition temperature.

^d Transition temperature from an isotropic or anisotropic liquid to a solid.

Table III. Transition Temperatures of (n-Alkyl β -D-Cellobioside) Hepta-n-alkanoates $A_mC_bHA_m$.^a

m	heating mode		cooling mode	
	T_{sl} ($^{\circ}C$)	T_{al} ($^{\circ}C$)	T_{la} ($^{\circ}C$)	T_{ls} ($^{\circ}C$)
8	41.5	93.5	81.8	16.1
9	48.0	93.7	88.6	25.0
10	62.5	95.0	90.7	39.5
12	72.5	92.6	88.6	38.9
14	84.2		76.3	57.0
16	81.2		80.7	68.4
18	84.1		75.9	71.3

^a See Table I for abbreviations.

Figure 6 gives similar data for $A_mC_bHA_m$. This series of derivatives also form an anisotropic phase for appropriate values of m, the region of which extends somewhat larger than that of $A_{10}C_bHA_m$ along both the temperature- and m-axes. The fine dotted lines in Figure 6b show the transition temperatures of C_bOA_m , cellobiose octaalkanoate⁵⁾, which structurally differs from $A_mC_bHA_m$ only in the l-O linkage, i.e., ester vs. ether. It is rather surprising that this small difference can produce the significant differences in the mesophase behavior. We recently prepared octa-O-alkyl- β -D-cellobiosides OA_mC_b , fully etherified cellobioses, which were found to have a very low ($< -20^{\circ}C$) solid-liquid transition temperature and form no mesophase for any value of m. This suggests that carboxyl groups, rather than molecular shapes, play an essential role in the mesophase formation of cellobiosic alkanoates.

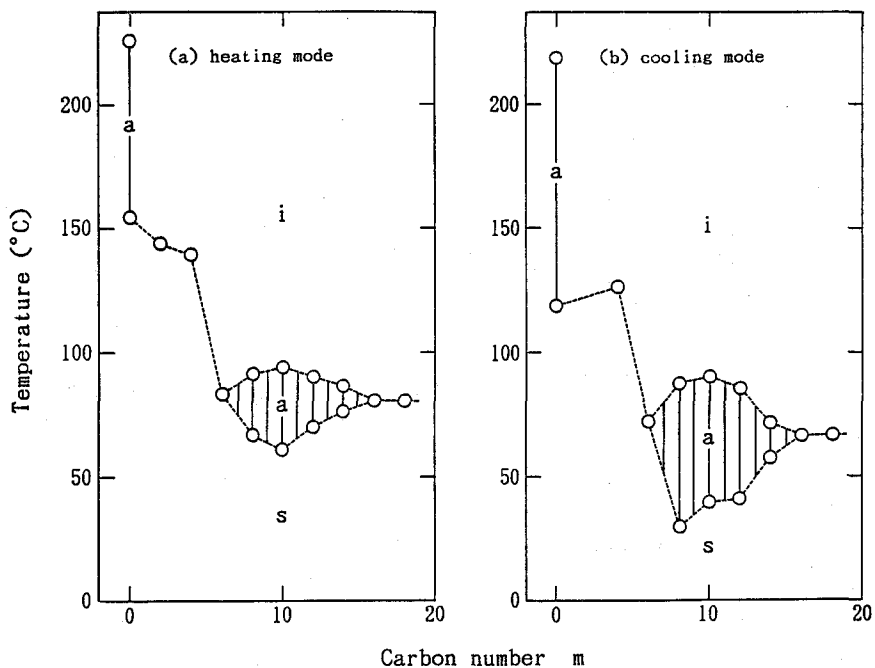


Fig. 5. Transition temperatures of $A_{10}C_6HA_m$. The, i, a, and s denote an isotropic, anisotropic, and solid phase, respectively.

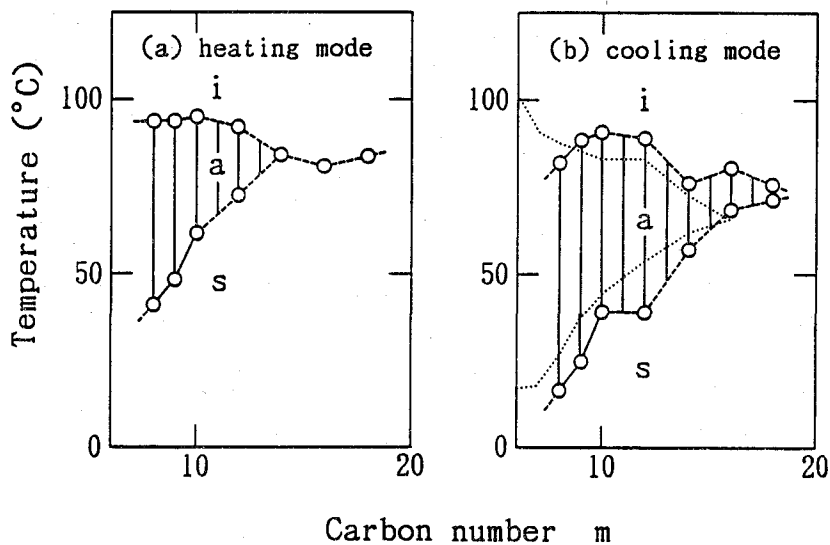


Fig. 6. Transition temperatures of $A_mC_6HA_m$ (cf. Figure 5). The fine dotted lines are for C_6OAm^{59} .

At the present time, we cannot give definite classifications of the alkanoates' mesophases. The similarities in textural, thermal, and physical properties among the three kinds of alkanoates $A_{10}C_bHA_m$, $A_mC_bHA_m$, and C_bOA_m (regarding textural similarities, compare, e.g., Figure 2 with Figure 2 in ref. 5) suggest that they all belong to the same smectic class, perhaps, of columnar type⁷⁾.

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